

(dd, $J = 14.2, 8.1$ Hz, H-7 β), 2.75 (dd, $J = 14.2, 9.0$ Hz, H-7 α), 3.02 (s, 3 H), 3.20 (d-like m, 2 H-10), 3.40-3.50 (m, 2 H-18), 3.88 (s, 3 H), 4.15 (q, $J = 6.9$ Hz, 2 H), 4.39 (br t, $J = 8.5$ Hz, H-8), 5.05 (s, H-5), 5.90 (m, H-9), 6.69 (s, H-1 and 2), 7.42 (s, H-16). The ^{13}C NMR (CDCl_3) spectrum of **7** was very similar to that of **5** except for the new appearance in **7** of a carbonyl signal [$\delta 205.8$ (s, C-6)] and a methylene signal $\delta 44.4$ (t, C-7)] at the cost of two olefinic signals [$\delta 102.2$ (d) and 150.5 (s)] and a methyl signal [$\delta 50.2$ (q)] in **5**.

The above results can be most reasonably explained by the stepwise mechanism involving ionic species shown in Scheme I, which was also compatible with the observation of remarkable solvent effects. The reaction may be initiated by the nucleophilic addition of **1** to the electron-deficient acetylenes¹⁴ followed by the cleavage of C(9)-N bond, which is stereoelectronically favored by its almost parallel arrangement to the p orbitals of adjacent C(8)=C(14) double bond. The sterically most favorable ring closure at C(8) position of the resulting intermediates (A and/or B) leads to the formation of adducts **4** and **5**.

The facile formation of a new type of adduct of **1**, by using polar solvents, is most noteworthy. These results provide a further way for chemical modifications of **1** and stimulate the reexamination of cycloaddition reactions of **1** with various dienophiles in different solvents, which is currently under way in our laboratory.

(13) Compound **8**: mp 231-233 °C (ethyl acetate); MS, m/e 381 (M^+); IR (Nujol) 1735 and 1670 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.68-2.00 (m, 2 H), 2.50 (dd, $J = 13.8, 8.0$ Hz, H-7 β), 2.82 (dd, $J = 13.8, 9.0$ Hz, H-7 α), 3.00 (s, 3 H), 3.18 (d-like m, 2 H), 3.40-3.60 (m, 2 H), 3.67 (s, 3 H), 3.86 (s, 3 H), 4.37 (br t, $J = 8.5$ Hz, H-8), 5.03 (s, H-5), 5.90 (m, H-9), 6.88 (s, H-1 and H-2), and 7.40 (s, H-16); ^{13}C NMR (CDCl_3) δ 29.2 (t), 37.4 (d), 37.4 (s), 41.5 (t), 44.5 (d) 51.1 (q), 53.3 (t), 54.2 (t), 56.5 (q), 89.4 (d), 105.4 (s), 112.8 (d), 119.6 (d), 126.3 (d), 126.3 (s), 132.2 (s), 138.5 (s), 142.3 (s), 143.9 (s), 150.6 (d), 169.4 (s), and 205.7 (s).

(14) Ethyl acrylate was found not to react with **1** in a similar way, but to give the Diels-Alder adduct under more drastic conditions.³

Generation and Recycle Use of Selenenylating Reagents in Electrochemical Oxyseleenylation-Deselenenylation of Olefins

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Oxyseleenylation-oxidative deselenenylation sequence provides double-bond transpositioned allylic alcohols and ethers from olefins.¹ The current method involves two steps: oxyseleenylation with PhSeX ($\text{X} = \text{Cl}, \text{Br}, \text{OR}, \text{and NR}_2$) followed by oxidation with O_3 , NaIO_4 , and peroxides (H_2O_2 , $t\text{-BuOOH}$, $m\text{-CPBA}$) where stoichiometric amounts of PhSeX in the former step and large excess amount of oxidative reagents in the latter are required.^{1,2} In principle, electrochemical transformation (**1** \rightarrow **3**) must be realized since both oxyseleenylation and deselenenylation via selenoxide are oxidative processes.³ Here, we describe a one-step preparation of allylic derivatives **3** from isoprenoids **1**, which is characterized by (1) electrochemical generation and recycled use of selenenylating reagents from a catalytic amount

Scheme I

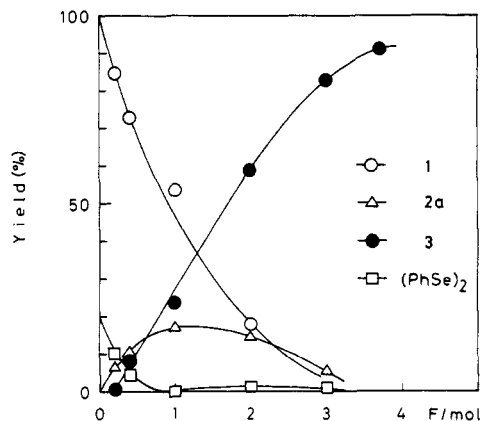
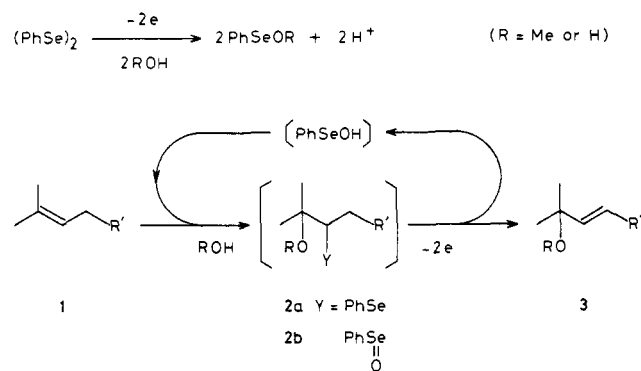


Figure 1. Electricity (F/mol of **1**) and yields of products [**2a** and **3**, $\text{R} = \text{CH}_2\text{CMe}(\text{OAc})\text{C}\equiv\text{CH}$] in the presence of 10 mol % of diphenyl diselenide in MeOH at 60-63 °C.

of diphenyl diselenide, (2) one-step preparation of allylic alcohols **3** ($\text{R} = \text{H}$) without use of phenylselenenic acid⁴ and selenenamide,⁵ and finally (3) deselenenylation in the absence of peroxides.

The reaction procedure requires a mixture of **5** (0.5 mmol), $(\text{PhSe})_2$ (0.05 mmol), and MgSO_4 (2.5 mmol) in $\text{MeCN}-\text{H}_2\text{O}$ (5:2) which is electrolyzed under a constant current (6.7 mA/cm², 4.2 F/mol) by using Pt foils as electrodes in an undivided cell at 66-68 °C, affording **14** ($\text{R} = \text{H}$, 89%). The results of the electrochemical transformation are summarized in Table I. Most of terminal ω double bonds of isoprenoids undergo regioselective oxyseleenylation-deselenenylation to give *trans*-allylic alcohols⁶ in aqueous acetonitrile and methyl ethers⁶ in methanol. Particularly noteworthy is the fact that the hydroxylyative double-bond transposition (**1** \rightarrow **3**, $\text{R} = \text{H}$) takes place efficiently in aqueous acetonitrile, which is an easier access to allylic alcohol **3** ($\text{R} = \text{H}$) than the known methods by phenylselenenic acid⁴ and phenylselenenamide.⁵ Acetoxy, carbomethoxy, ethynyl, and sulfonyl groups are inert in the electrolytic conditions. Enol acetate **10** was converted into α,β -unsaturated ketone **19** (81%) by this procedure. β -Pinene **11** provided **20a** and **20b** via oxyseleenylation involving ring opening of the cyclobutane skeleton^{3b} \rightarrow selenoxylation \rightarrow [2,3]-sigmatropic rearrangement of the selenoxide.^{1,7} This electrochemical reaction can be demonstrated by a one-step synthesis of *dl*-dihydroactinidiolide **21** (92%)⁸ from

(1) (a) Clive, D. L. J. *Tetrahedron* 1978, 34, 1049. (b) Reich, H. J. *Acc. Chem. Res.* 1979, 12, 22.

(2) For instance, the transformation (**1** \rightarrow **3** for citronellol, $\text{R} = \text{H}$) is performed by the action of 3 mol equiv of PhSeOH for hydroxyseleenylation followed by 5 mol equiv of $t\text{-BuOOH}$ for deselenenylation via selenoxide: Hori, T.; Sharpless, K. B. *J. Org. Chem.* 1978, 43, 1689.

(3) We reported recently a bromide ion mediated electrochemical oxyseleenylation: (a) Torii, S.; Uneyama, K.; Handa, K. *Tetrahedron Lett.* 1980, 21, 1863. (b) Torii, S.; Uneyama, K.; Ono, M. *Ibid.* 1980, 21, 2741. (c) Torii, S.; Uneyama, K.; Ono, M. *Ibid.* 1980, 21, 2653.

(4) (a) Hölzle, G.; Jenny, W. *Helv. Chim. Acta* 1958, 41, 593. (b) Sharpless, K. B.; Lauer, R. F. *J. Org. Chem.* 1974, 39, 429. (c) Reich, H. J. *Ibid.* 1974, 39, 428. (d) Clive, D. L. J. *J. Chem. Soc., Chem. Commun.* 1974, 100.

(5) (a) Nicolaou, K. C.; Claremon, D. A.; Barnette, W. E.; Seitz, S. P. *J. Am. Chem. Soc.* 1979, 101, 3704. (b) Reich, H. J.; Renga, J. M. *J. Org. Chem.* 1975, 40, 3313.

(6) Purity of **3** was determined by HPLC (μ -Porasil, *n*-hexane-ethyl acetate 5:1). The coupling constants of the newly formed double bond (J , Hz) are as follows: **13**, 15.7; **14**, 15.6; **15**, 15.4; **16**, 15.4; **17**, 15.1; **18**, 15.9; **19**, 15.9.

(7) Reich, H. J. *J. Org. Chem.* 1975, 40, 2570.

Table I. Electrooxidative Oxyseleenylation-Deselenenylation of Olefins

	substrate	F/mol ^a	product	R	yield, % ^b
4		5.6 3.6	13	Me H	82 80
5		3.7 4.2	14	Me H	91 89
6		3.1 5.9	15	Me H	79 81
7		3.9 6.0	16	Me H	86 69
8		4.8	17	Me	73
9		9.3	18	H	73 ^c
10		11.9	19	—	81 ^c
11		4.0	20	a R; C(Me) ₂ OMe b R; C(Me)=CH ₂	61 13
12		8.2	21		92 ^d

^a Electricity passed during the electrolysis, F/mol of substrate 1. Theoretically, 3 F/mol of electricity is required for the transformation (1 → 3). ^b Isolated yield using 10 mol % of diphenyl diselenide. ^c 20 mol % of diphenyl diselenide was used. ^d 50 mol % of diphenyl diselenide was used.

carboxylic acid 12. The lactone 21 would be produced by electrochemical intramolecular oxyseleenylation followed by electrochemical selenoxylolation and elimination of phenylselenenic acid.⁹

The electrooxidatively generated phenylselenenyl reagents (PhSeOR, R = H or Me, Scheme I)¹⁰ reacts regioselectively with olefins producing oxyseleenylation 2a at the first step, followed by the subsequent electrochemical oxidation of 2a to provide the corresponding selenoxide 2b, which instantaneously undergoes syn

elimination¹¹ to give the desired product 3.^{12,13} As shown in Figure 1 2a [R' = CH₂CMe(OAc)C≡CH] increased gradually, reached the optimum amount near 1 F/mol, and completely disappeared at 3.7 F/mol. Diphenyl diselenide was consumed within 1 F/mol;¹⁴ however, the starting material 1 decreased gradually and the final product 3 increased steadily on further electrolysis. These results suggest that a selenenylation reagent is regenerated in situ and promotes the transformation (1 → 3). It is noteworthy that electrooxidation of a mixture [84% of 1 and 16% of 2a, R' = CH₂CMe(OAc)C≡CH] in the absence of diphenyl diselenide in MeOH provided 3 in 63% yield after 7.6 F/mol, revealing clearly

(8) (a) Sakan, T.; Isoc, S.; Hyeon, S. B. *Tetrahedron Lett.* **1967**, 1623. (b) Uneyama, K.; Kuyama, M.; Torii, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2108 and references cited therein.

(9) A solution of 12 (0.2 mmol), (PhSe)₂ (0.1 mmol), Et₄NBr (0.05 mmol), and Na₂CO₃ (0.2 mmol) dissolved in MeCN (7 mL)-H₂O (0.2 mL) was electrolyzed at room temperature (70 mA for 36 min, 8.2 F/mol) giving 21. While, an intramolecular oxyseleenylation product, 2,2,6-trimethyl-1-(phenylseleno)-7-oxabicyclo[4.3.0]nonan-8-one was prepared by the action of 12 with phenylselenenyl bromide in CH₂Cl₂ and subjected to electrolysis, providing 21. The spectral data of synthetic 21 was consistent with those of the authentic sample.⁸

(10) Polarographic analysis showed that diphenyl diselenide is oxidized at 0.96 V vs. Ag/Ag⁺ in MeCN where olefin 1 could not be oxidized. Bewick, A.; Coe, D. E.; Fuller, G. B.; Mellor, J. M. *Tetrahedron Lett.* **1980**, 3827.

(11) (a) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (b) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1697.

(12) The presence of small amounts of sulfuric acid using stoichiometric amount of diphenyl diselenide suppresses selenoxylolation of 2a and enabled us to prepare 2a chemoselectively.^{3a,b}

(13) Although the corresponding selenoxide 2b derived from 4-12 were not isolated due to the fast syn elimination, the selenoxide, 2-methoxy-1-(phenylselenenyl)octane, derived from electrolysis of 1-octene, was actually isolated and identified spectroscopically in comparison with the authentic sample.

(14) At this stage the yellow color of diphenyl diselenide in the reaction solution almost faded away.

that phenylselenenic acid generated from syn elimination of the corresponding selenoxide is recycled during the electrolysis. Therefore, the electricity required for the total conversion is effectively saved.¹⁵

The effect of salts such as MgSO_4 , CaSO_4 (82%), Na_2SO_4 (86%), K_2SO_4 (65%), SrSO_4 (51%), BaSO_4 (54%), and $\text{Mg}(\text{ClO}_4)_2$ (63%) is remarkable for the recycle, since the yield of **14** was only 26% in the absence of these salts and 10 mol % of diphenyl diselenide to **5** was employed. It is reasonable to assume that these salts prevent the conversion of phenylselenenic acid into inert phenylseleninic acid both by disproportionation¹⁶ and in part by electrooxidation,¹⁷ although the detailed mechanism of the effect is not yet clear.¹⁸

(15) For instance, electrolysis of **5** in the presence of stoichiometric amount of diphenyl diselenide requires almost twice the amount of electricity (7.8 F/mol) in MeOH although the yield is slightly better (91% \rightarrow 95%, Table I).

(16) (a) Behaghel, O.; Seibert, H. *Chem. Ber.* 1933, 66, 708. (b) Reference 11b.

(17) After electrolysis phenylseleninic acid was extracted with aqueous Na_2CO_3 and was converted into diphenyl diselenide by reduction with NaHSO_3 .²

(18) A study on the mechanism of the recycle and the electrode process of diphenyl diselenide in the present electrolysis system is going on. The details will be reported elsewhere.

Stereomutation at Pentacoordinate Silicon by Intramolecular Ligand Exchange

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Although anionic, pentacoordinate silicon species have received some attention,¹ detailed studies describing both structure and ligand exchange processes have not been reported. We wish to present the first direct evidence for stereomutation of a pentacoordinate silicon compound by intramolecular ligand exchange.

The spiro siliconate **1**,² prepared by reaction of **3**^{1a} with tris(dimethylamino)sulfonium (TAS) trimethyldifluorosilicate³ (Scheme I), exhibits a temperature-dependent ¹⁹F NMR spectrum. The $\text{A}_3\text{A}_3'\text{B}_3\text{B}_3'\text{X}$ pattern observed in the limiting low-temperature spectrum (-15°C) is transformed to a simple A_{12}X pattern (at 70°C) when interchange of diastereotopic trifluoromethyl groups is sufficiently rapid.⁴ Visual fit of observed and calculated⁵ spectra

† Contribution No. 2904.

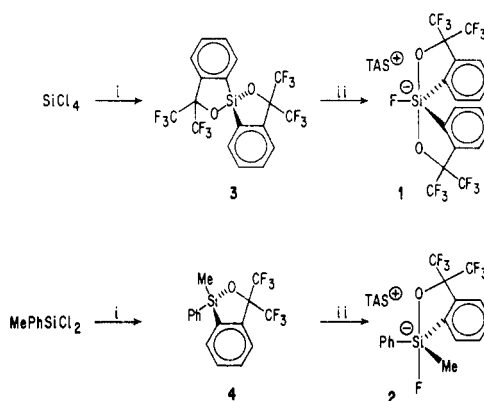
(1) (a) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* 1979, 101, 1591. (b) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* 1968, 7, 155. (c) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* 1977, 55, 1167. (d) Corriu, R. J. P.; Royo, G.; De Saxcé, A. *J. Chem. Soc., Chem. Commun.* 1980, 892. (e) Boer, F. P.; Flynn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* 1968, 90, 6973. (f) Boer, F. P.; van Remoortere, F. P. *Ibid.* 1970, 92, 801. (g) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* 1974, 2051. (h) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* 1981, 103, 480. (i) Brelie, C.; Carre, F.; Corriu, R. J. P.; De Saxcé, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* 1981, 205, Cl. (j) Frye, C. L. *J. Am. Chem. Soc.* 1970, 92, 1205.

(2) mp $141\text{--}142^\circ\text{C}$. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_3\text{O}_2\text{F}_{13}\text{SSi}$: C, 41.44; H, 3.77; N, 6.04. Found: C, 41.81; H, 3.84; N, 5.91. Molecular weight determined by osmometry in 1,2-dichloroethane was 650.

(3) Middleton, W. J. (to Du Pont) U.S. Patent 3940402. Tris(dimethylamino)sulfonium trimethyldifluorosilicate was prepared according to the following procedure. Sulfur tetrafluoride (0.12 mol) was condensed in a flask charged with dry ether (150 mL). (Dimethylamino)trimethylsilane (0.37 mol) was added dropwise to the mixture at -78°C . The mixture was warmed slowly to 25°C and stirred for 72 h in an atmosphere of dry nitrogen. Filtration under nitrogen provided a nearly quantitative yield of white solid, mp $58\text{--}62^\circ\text{C}$.

(4) (1) ¹⁹F NMR (-15°C , CD_3CN) ϕ_A -74.80 , ϕ_B -75.05 , ϕ_X -130.1 , $J_{AB} = 9.2$ Hz, $J_{AX} \sim 3.5$ Hz, $J_{BX} \sim 1.5$ Hz; (70°C) ϕ_A -74.93 , ϕ_X -130.1 , $J_{AX} = 2.5$ Hz (13 line pattern).

Scheme I^a



^a (i) Dilithium reagent from hexafluorocumyl alcohol and 2 equiv of *sec*-butyllithium. (ii) $(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$ in acetonitrile; TAS = $(\text{Me}_2\text{N})_3\text{S}$.

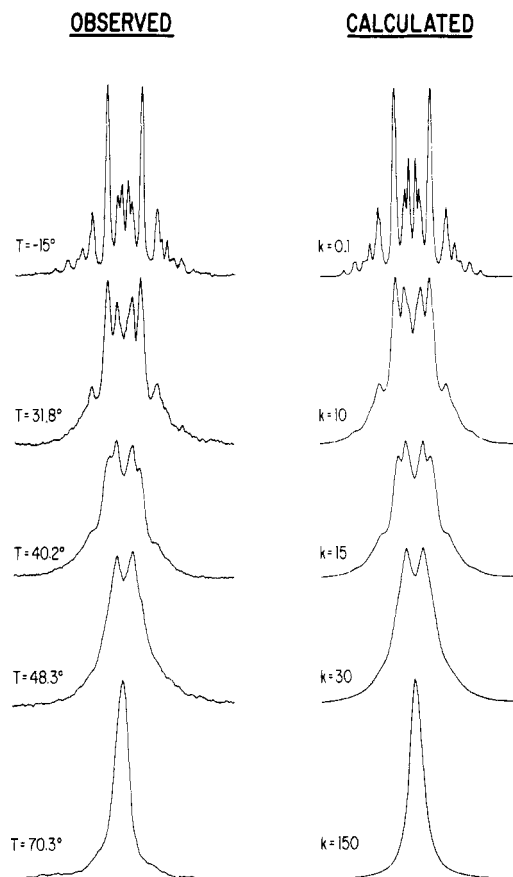


Figure 1. Representative observed and calculated ¹⁹F NMR spectra for **1** (CF_3 region). Spectra were recorded while decoupling protons and the silicon-bound fluorine nucleus.

at various temperatures provided $\Delta G^\ddagger = 16.6$ kcal/mol ($\Delta H^\ddagger = 14.1$ kcal/mol; $\Delta S^\ddagger = -8$ eu) (Figure 1). Spectra were concentration independent and, except for minor differences in $\Delta\nu$, were solvent independent (acetonitrile, 1,2-dichloroethane). The exchange rate was unchanged by addition of either hexamethylphosphoramide or hexamethyldisilazane (HMDS).⁶ That

(5) Spectra were calculated by using LAOCOON 3 and DNMR 3 programs. Kleier, D. A.; Binsch, G. "DNMR3: A Computer Program for the Calculation of Complex Exchange-Broadened NMR Spectra. Modified Version for Spin Systems Exhibiting Magnetic Equivalence or Symmetry," Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970. See also: *J. Magn. Reson.* 1970, 3, 146.

(6) HMDS was added to remove trace amounts of water or acid which might be present.